Global Lifetime of Elemental Mercury Against Oxidation by Atomic Bromine in the Free Troposphere

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Global lifetime of elemental mercury against oxidation by atomic bromine in the free troposphere

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[1] We calculate the global mean atmospheric lifetime of elemental mercury (Hg^0) against oxidation by atomic bromine (Br) in the troposphere by combining recent kinetic data for the Hg-Br system with modeled global concentrations of tropospheric Br. We obtain a lifetime of 0.5–1.7 years based on the range of kinetic data, implying that oxidation of Hg^0 by Br is a major, and possibly dominant, global sink for Hg^0. Most of the oxidation takes place in the middle and upper troposphere, where Br concentrations are high and where cold temperatures suppress thermal decomposition of the HgBr intermediate. This oxidation mechanism is consistent with mercury observations, including in particular high gaseous Hg(II) concentrations in Antarctic summer. Better free-tropospheric measurements of bromine radicals and further kinetic study of the Hg-Br system are essential to more accurately assess the global importance of Br as an oxidant of atmospheric Hg^0. **Citation:** Holmes, C. D., D. J. Jacob, and X. Yang (2006), Global lifetime of elemental mercury against oxidation by atomic bromine in the free troposphere, *Geophys. Res. Lett.*, *33*, L20808, doi:10.1029/2006GL027176.

[2] Mercury is present in the atmosphere principally in its elemental form, Hg^0, which can be transported globally, as indicated by the uniformity of its atmospheric concentration. Hg^0 is eventually oxidized to Hg(II), which may cycle back to Hg^0, partition into atmospheric water, or react with surfaces. The latter two processes contribute to mercury deposition and accumulation in ecosystems. Some deposited mercury is subsequently reduced and re-emitted as Hg^0. Unlike other heavy metals, mercury transits among surface reservoirs primarily through atmospheric fluxes [*Mason and Sheu*, 2002]. Therefore, understanding the atmospheric redox chemistry of mercury is critical to determining source-receptor relationships of this toxic element.

[3] Current models assume that gaseous hydroxyl radicals (OH) and gaseous ozone (O_3) are the main global oxidants of Hg^0 [e.g., *Bergan and Rodhe*, 2001]. Laboratory kinetic studies imply that the global mean lifetime of Hg^0 is 120–210 days against oxidation by OH [*Sommar et al.*, 2001; *Pal and Ariya*, 2004a] and 60–1500 days against oxidation by O_3 [*Hall*, 1995; *Pal and Ariya*, 2004b]. However, in light of the expected rapid thermal dissociation of HgOH [*Goodsite et al.*, 2004], *Calvert and Lindberg* [2005] concluded that oxidation of Hg^0 by OH is much slower than reported by the above studies and is insignificant under atmospheric conditions. Atmospheric observations constrain the residence time of total atmospheric mercury (Hg^0 + Hg(II)) to 0.5–2 years [*Schroeder and Munthe*, 1998], which places an upper limit on the lifetime of Hg^0 against oxidation (depending on competition between reduction and deposition of Hg(II)). Ozone alone cannot be the main oxidant of Hg^0 because it explains neither the observed seasonal variation of Hg^0 and dissolved Hg(II) in rainwater [*Bergan and Rodhe*, 2001; *Selin et al.*, 2006], nor the observed diurnal cycle of gaseous Hg(II) [*Laurier et al.*, 2003; *Hedgecock et al.*, 2005]. These observations imply that oxidation of Hg^0 must be photochemically mediated.

[4] *Goodsite et al.* [2004] developed a homogeneous mechanism for Hg-Br chemistry in the troposphere based on theoretical kinetic calculations, and showed that gas-phase oxidation of Hg^0 by Br atoms could explain mercury depletion events (MDEs) in the Arctic springtime boundary layer. They suggested that this mechanism would be important more generally in the marine boundary layer and on the global scale. *Lin et al.* [2006] suggested that Hg-Br chemistry is also significant in the upper troposphere. We present here a quantitative analysis of the global lifetime of Hg^0 against oxidation by tropospheric Br by combining the mechanism of *Goodsite et al.* [2004] with Br concentrations from a global 3-D simulation of tropospheric bromine chemistry [*Yang et al.*, 2005] as well as updated kinetic data. We find that oxidation by Br in the middle and upper troposphere could be an important sink for Hg^0, and that the mechanism yields an atmospheric lifetime of Hg^0 consistent with observational constraints.

[5] Recent observations indicate that the free troposphere contains significant BrO. Satellite instruments (GOME and SCIAMACHY) observe BrO columns with $1-4 \times 10^{13}$ molecules cm^{-2} in excess of the known stratospheric abundance [*Salawitch et al.*, 2005; *Sinnhuber et al.*, 2005]. This corresponds to 0.5–2 pptv BrO distributed throughout the tropospheric column. Balloon measurements in the northern mid-latitudes and tropics give independent evidence for 0.5–2 pptv BrO in the troposphere [*Fitzenberger et al.*, 2000; *Pundt et al.*, 2002; *Van Roozendael et al.*, 2002]. Tropospheric sources include activation from sea salt; oxidation and photolysis of bromocarbons; transport from the stratosphere; and recycling from reservoir species (Br_2, HOBr, $BrNO_2$, $BrONO_2$, HBr) by homogeneous and heterogeneous processes [*von Glasow et al.*, 2002; *Platt and Honninger*, 2003; *Yang et al.*, 2005; *Salawitch*, 2006].

[6] Some ground-based observations have found lower abundances of tropospheric BrO. *Schofield et al.* [2004] found an upper limit of 1.2×10^{13} molecules cm^{-2} in the

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Table 1. Rate Constants for Oxidation of Hg^0 by Br Under Atmospheric Conditions

	Rate Constant[a]	Conditions	Reference
k_1	3.2×10^{-12}	1 atm, 298K	[*Ariya et al.*, 2002]
	$1.0 \times 10^{-12} \exp(209/T)$	1 atm[b]	[*Khalizov et al.*, 2003]
	$1.1 \times 10^{-12} (T/298)^{-2.37}$	1 atm[b]	[*Goodsite et al.*, 2004]
	$3.0–9.7 \times 10^{-13}$	1 atm, 298K[c]	[*Donohoue et al.*, 2006]
	$1.5 \times 10^{-32} (T/298)^{-1.86}$ [M]		[*Donohoue et al.*, 2006]
k_2	$1.2 \times 10^{10} \exp(-8357/T)$	1 atm	[*Goodsite et al.*, 2004]
$k_{3,Br}$	$2.5 \times 10^{-10} (T/298)^{-0.57}$	1 atm, high p limit	[*Goodsite et al.*, 2004]
	3.0×10^{-11}	2 body, 298K[d]	[*Balabanov et al.*, 2005]
	1.2×10^{-10}	high p limit, 298K	[*Balabanov et al.*, 2005]
$k_{3,OH}$	$2.5 \times 10^{-10} (T/298)^{-0.57}$	1 atm, high p limit[e]	[*Goodsite et al.*, 2004]
k_4	3.9×10^{-11}	298K	[*Balabanov et al.*, 2005]

[a]Rate constants are in units of cm^3 $molecule^{-1}$ s^{-1}, except for k_2 (s^{-1}). T is temperature in K. [M] is the number density of air.
[b]We assume in our calculations that k_1 is in the low-pressure regime at 1 atm, following *Donohoue et al.* [2006], and thus scale k_1 with [M].
[c]Unpublished data from *Spicer et al.* [2002] cited by *Donohoue et al.* [2006].
[d]Rate constant in the absence of a third body, i.e., with stabilization of the activated complex solely by internal energy dissipation.
[e]Inferred by analogy with $k_{3,Br}$.

tropospheric column over Lauder, New Zealand. The maximum tropospheric column observed by *Leser et al.* [2003] during an Atlantic cruise was 0.6×10^{13} molecules BrO cm^{-2}. However, neither method was sensitive to BrO near the tropopause and therefore both could be reconciled with satellite observations if much of the satellites' nominally tropospheric BrO column were concentrated in the upper troposphere or lowermost stratosphere [*Salawitch et al.*, 2005].

[7] *Raofie and Ariya* [2004] reported a gas-phase reaction of BrO with Hg^0, but could not exclude the possibility of heterogeneous mechanisms in their experimental system. Homogeneous oxidation of Hg^0 by BrO is endothermic and has a large energy barrier, making its atmospheric relevance unlikely [*Balabanov and Peterson*, 2003; *Tossell*, 2003]. However, oxidation by Br atoms is fast [*Calvert and Lindberg*, 2004; *Goodsite et al.*, 2004]. Rapid chemical cycling between BrO and Br through BrO photolysis, self-reaction, and reaction with NO, balanced by Br oxidation by O_3, maintains Br:BrO molar ratios of 0.01–2 in the daytime troposphere [*Platt and Janssen*, 1995; *Yang et al.*, 2005].

[8] We estimate here the global impact of atomic bromine on atmospheric oxidation of mercury through the two-step recombination reactions (R1) + (R3), in competition with thermal dissociation (R2), following *Goodsite et al.* [2004]:

(R1) $$\mathrm{Hg + Br \xrightarrow{M} HgBr}$$

(R2) $$\mathrm{HgBr \xrightarrow{M} Hg + Br}$$

(R3) $$\mathrm{HgBr + X \xrightarrow{M} HgBrX} \qquad (\mathrm{X = Br, OH})$$

Other species (e.g., X = I, O_2) may also contribute to reaction (R3) [*Goodsite et al.*, 2004], but their effect is probably minor and we disregard them. The local lifetime of Hg^0 against oxidation to chemically stable Hg(II) by (R1)–(R3) is

$$\tau_{local} = \frac{k_2 + k_{3,Br}[Br] + k_{3,OH}[OH]}{k_1[Br]\left(k_{3,Br}[Br] + k_{3,OH}[OH]\right)}. \quad (1)$$

Table 1 compiles literature values of k_1, k_2, and k_3. Reaction (R2) makes τ_{local} extremely sensitive to temperature, as k_2 doubles with every increase of 6 K (at 273K) [*Goodsite et al.*, 2004]. There is limited information about the temperature (T) and pressure (p) dependences of k_1 and k_3. *Donohoue et al.* [2006] found that reaction (R1) is in the low pressure regime for $p \leq 1$ atm. *Balabanov et al.* [2005] reported high and low pressure limits for $k_{3,Br}$, while *Goodsite et al.* [2004] found that the reaction is in the high pressure regime at 1 atm.

[9] We calculate the global mean tropospheric lifetime of Hg^0 against conversion to Hg(II) by (R1)–(R3) by integrating the loss over the troposphere using global distributions of Br, OH, and temperature, and assuming a uniform tropospheric Hg^0 mixing ratio. For the Br concentration, we use monthly and zonally averaged values for four months (January, April, July, and October) from the global chemical transport model (CTM) of tropospheric bromine described by *Yang et al.* [2005] (Figure 1). This model includes budgets of the dominant bromocarbons and an empirical parameterization of halogen release from sea salt aerosols based on wind speed and observed bromide depletion. It simulates daytime tropospheric BrO columns (0.2–1.6×10^{13} molecules cm^{-2}) that are at the low end of the range of satellite observations; thus, the model provides a conservative, process-based estimate of bromine abundance. We use monthly mean temperatures from the NASA Goddard Earth Observing System (GEOS-4) assimilated meteorology for 1999. Monthly mean OH distributions are from a detailed simulation of tropospheric chemistry [*Park et al.*, 2004]. OH and Br are present only during daylight, so we distribute the average monthly concentrations over the daytime hours.

[10] Partitioning among inorganic bromine species explains much of the variability of atomic Br in Figure 1 [*Yang et al.*, 2005]. Br constitutes 10% of inorganic bromine near the tropical tropopause, where HBr and $BrONO_2$ photolyze rapidly, but less than 1% near the surface. Seasonal changes in BrO photolysis increase atomic Br concentrations in the summer hemisphere. Atomic Br is generally more abundant in the southern hemisphere than in the north because high wind speeds over the southern ocean drive large emissions from sea salt aerosols.

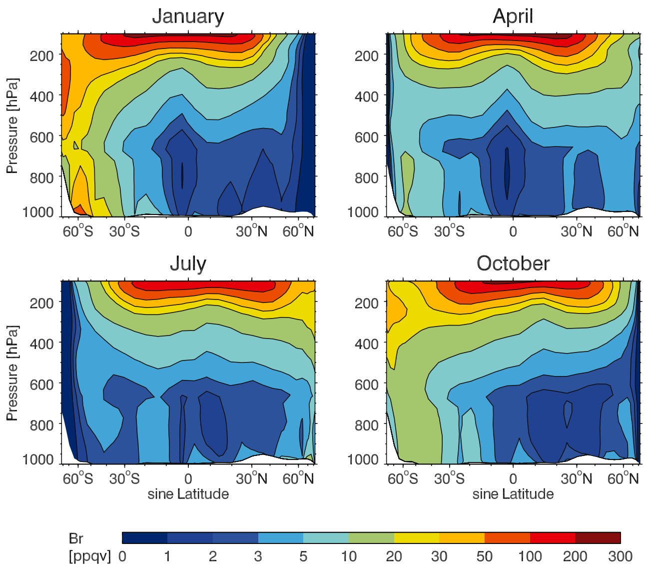

Figure 1. Monthly and zonally averaged atomic Br mixing ratios [ppqv] from the *Yang et al.* [2005] chemical transport model (CTM), which includes inorganic bromine released from sea salt and by photolysis and oxidation of bromocarbons. 1 ppqv = 10^{-15} mol mol^{-1}.

[11] Figure 2 shows the lifetime of Hg^0 against conversion to Hg(II) by (R1)–(R3), computed from Equation (1) for the months of January, April, July, and October. For this 'base case' estimate we use the most recent kinetic data with T and p dependences: k_1 from *Donohoue et al.* [2006]; $k_{3,Br}$ and $k_{3,OH}$ from *Goodsite et al.* [2004]; and k_2 calculated to maintain the k_1:k_2 balance [*Goodsite et al.*, 2004].

[12] From Figure 2 we see that the lifetime of Hg^0 is less than 300 days in all seasons near the tropical tropopause due to high Br concentrations and low temperatures (suppressing (R2)). This is consistent with recent aircraft observations of high concentrations of aerosol-bound mercury (presumably Hg(II)) associated with bromine and iodine near the tropopause [*Murphy et al.*, 2006]. Assuming a uniform mixing ratio of Hg^0 up to the tropopause (taken as 150 hPa in the tropics and 300 hPa elsewhere), we find that 47% of Hg^0 tropospheric oxidation occurs in the upper troposphere (above 500 hPa), 32% in the middle troposphere (800–500 hPa), and 21% in the lower troposphere. The lifetime we calculate for the northern mid-latitude boundary layer (>500 days) is much longer than a previous lower bound of 160 days for the marine boundary layer in that region [*Goodsite et al.*, 2004] mainly because our zonal-mean lifetime accounts for the lower Br abundances over land. The seasonal cycle in Figure 2 shows that despite the opposing influence of temperature, the increased concentrations of Br and OH in summer shorten τ_{local} relative to winter, in agreement with the observed seasonal cycle of Hg^0 [e.g., *Ebinghaus et al.*, 2002; *Selin et al.*, 2006].

[13] Mass-weighted integration of the Hg^0 loss rates ($1/\tau_{local}$) from Figure 2 yields a global mean tropospheric Hg^0 lifetime, τ_{global}, of 510 days against conversion to Hg(II) by (R1)–(R3). This is similar to current estimates of the lifetime of Hg^0 against oxidation by ozone [e.g., *Selin et al.*, 2006] and could account for a large part of the Hg^0 loss within the 0.5–2 yr observational constraint on the atmospheric lifetime of total mercury. We find that ~85% of the Hg(II) formed is HgBrOH. This assumes, following *Goodsite et al.* [2004], that the value of $k_{3,OH}$ is the same as that of $k_{3,Br}$ which they explicitly calculated. If reaction (R3) with OH were insignificant (i.e., $k_{3,OH}$ = 0) then the global Hg^0 lifetime would be 50% greater, with the largest changes in the lower troposphere.

[14] Our calculations predict rapid summertime oxidation of Hg^0 (τ_{local} = 10–100 days) at all altitudes in Antarctic summer. *Sprovieri et al.* [2002] and *Temme et al.* [2003] have observed high concentrations of gaseous Hg(II) on the Antarctic coast during November through January; these differ from springtime mercury depletion events in that they observe positive correlations between gaseous Hg(II) and ozone. As OH, O_3 and other known oxidants of Hg^0 could not explain the observed Hg(II) concentrations, *Sprovieri et al.* [2002] hypothesized a role for bromine radicals or photochemical oxidants generated immediately above the snowpack. S. Brooks et al. (Antarctic polar plateau snow surface conversion of deposited oxidized mercury to gaseous elemental mercury with fractional long-term burial, submitted to *Geophysical Research Letters*, 2006) also observed high gaseous Hg(II) at the South Pole under unstable atmospheric conditions, which they attributed to halogen reactions in the upper troposphere. Our work shows that subsiding air from any part of the troposphere could bring to the surface gaseous Hg(II), formed by reactions with Br, together with elevated ozone.

[15] Thus far our base case calculations have used one combination of rate constants (k_1 from *Donohoue et al.* [2006]; $k_{3,Br}$, $k_{3,OH}$, and k_1:k_2 from *Goodsite et al.* [2004]).

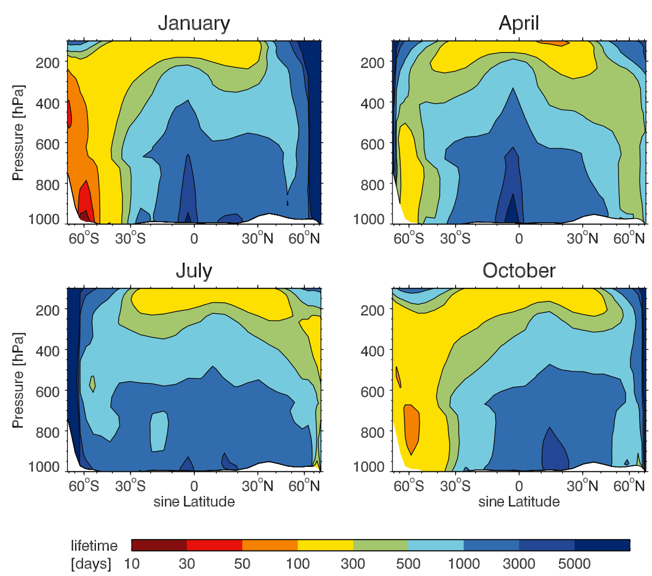

Figure 2. Lifetime [days] of atmospheric Hg^0 against oxidation to Hg(II) by two-step recombination with Br atoms and OH (reactions (R1)–(R3) forming $HgBr_2$ or HgBrOH), using 'base case' rate constants from *Donohoue et al.* [2006] and *Goodsite et al.* [2004] with the bromine distribution shown in Figure 1. The corresponding global-mean tropospheric lifetime of Hg^0 is 510 days, assuming a uniform Hg^0 mixing ratio. The text describes results with other rate constants from Table 1, all of which yield qualitatively similar distributions of Hg^0 lifetime.

Other theoretical [*Khalizov et al.*, 2003; *Goodsite et al.*, 2004] and experimental [*Ariya et al.*, 2002] estimates of k_1 are faster (see Table 1), although *Donohoue et al.* [2006] argue that these values are less accurate. The fastest k_1 value with reported temperature dependence [*Khalizov et al.*, 2003] implies τ_{global} = 160 days, after recalculating k_2 to keep the k_1:k_2 balance [*Goodsite et al.*, 2004].

[16] The calculated value of τ_{global} also depends on competition between reactions (R2) and (R3). *Balabanov et al.* [2005] studied reaction (R3) as well as several additional reactions that could occur in the Hg-Br system. Their high-pressure limit for $k_{3,\mathrm{Br}}$ is half that of *Goodsite et al.* [2004]. They also found that abstraction of Br from HgBr by reaction (R4) decreases the rate of Hg(II) formation.

$$\mathrm{HgBr} + \mathrm{Br} \rightarrow \mathrm{Hg} + \mathrm{Br_2} \qquad \text{(R4)}$$

Calculating the global lifetime of Hg^0 against reactions (R1)–(R4) with the high pressure k_3 and k_4 values from *Balabanov et al.* [2005], and other rates the same as our base case, yields τ_{global} = 630 days. Additional oxidants for HgBr in reaction (R3) suggested by *Balabanov et al.* [2005], such as BrO and Br_2, would decrease τ_{global}.

[17] The amount and distribution of tropospheric Br is a large uncertainty in our lifetime estimates. Our calculations show that in order to have a globally significant impact on Hg^0, atomic Br must be present in the middle and upper troposphere, where cold temperatures suppress the thermal dissociation of HgBr. While global models predict peak Br concentrations in this region from bromocarbon sources [*von Glasow et al.*, 2004; *Yang et al.*, 2005], observational evidence is indirect and does not clearly resolve the upper troposphere and lowermost stratosphere [*Salawitch et al.*, 2005]. Even in the lowermost stratosphere, atomic Br could significantly shorten the lifetime of Hg^0 through relatively rapid air exchange with the troposphere.

[18] In conclusion, oxidation by atomic bromine could result in an atmospheric lifetime of Hg^0 against conversion to Hg(II) of 1.4–1.7 years, and possibly as short as 0.5 years, with most reaction taking place in the free troposphere. This would be an important, and possibly dominant, global pathway for oxidation and deposition of atmospheric mercury. It could reconcile the atmospheric evidence that Hg^0 oxidation is photochemically mediated [*Bergan and Rodhe*, 2001; *Selin et al.*, 2006] with the evidence against a major role for oxidation by OH [*Calvert and Lindberg*, 2005]. The mechanism appears qualitatively consistent with mercury observations – the seasonal cycle of Hg^0; airborne particulate mercury measurements; and gaseous Hg(II) in Antarctic summer – but global CTMs are necessary for more stringent quantitative tests. Improved atmospheric measurements of inorganic bromine and its radicals, particularly in the middle and upper troposphere, are needed. Uncertainties in the kinetic data, especially for reactions involving HgBr as a reactant, need to be resolved in order to more narrowly constrain the lifetime of Hg^0 and the Hg(II) product distribution.

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